

POLYMERIZATION AND CHARACTERIZATION OF HIGH CONDUCTIVITY AND GOOD ADHENSION POLYPYRROLE FILMS FOR ELECTROMAGNETIC INTERFERENCE SHIELDING*

Yong-sheng Qiao^{a, b}, La-zhen Shen^{b**} and Tao Dou^a

^a *Institute of Special Chemicals, Taiyuan University of Technology, Taiyuan 030024, China*

^b *School of Chemistry and Chemical Engineering, Shanxi Datong University, Datong 037009, China*

Ming Hu^c

^c *School of Electronic Information Engineering, Tianjin University, Tianjin 300072, China*

Abstract Polypyrrole (PPy) shows a favorable application in the electromagnetic interference (EMI) shielding due to its good electrical conductivity and outstanding air stability. Conducting PPy films with high conductivity and good adhesion were successfully polymerized on the surface of insulating epoxy resin substrates using chemical polymerization. The factors affecting the properties of PPy films, such as the surface morphology, adhesion between PPy film and substrate, electrical conductivity, EMI shielding effectiveness (SE), were investigated. The adhesion was improved significantly through a three-step surface pretreatment of epoxy resin substrates including removing impurities, roughening, and surface modification with silane coupling agent. An enhancement in the conductivity of PPy films of about one order of magnitude was achieved by adding dopant in FeCl₃ solution. The higher the conductivity, the better the shielding effectiveness. Taking sodium *p*-toluenesulfonate doped PPy film as example, EMI SE was in the practically useful range of about 30 dB over a wide frequency range from 30 MHz to 1500 MHz. The PPy film samples were characterized by scanning electron microscopy (SEM), infrared spectra (IR), X-ray photoelectron spectroscopy (XPS) and the flange coaxial transmission device. The four-point probe method was used to measure conductivity of PPy films.

Keywords: Polypyrrole film; EMI; Conductivity; Adhesion.

INTRODUCTION

Polypyrrole (PPy) is considered one of the most investigated conducting polymers and also is the focus in many studies with various practical applications because of its high conductivity, outstanding air stability and special physical, chemical properties compared with other conducting polymers^[1–4]. PPy film is widely used in electronic device^[5], semiconductor apparatus^[6], biosensor^[7], polymeric battery^[8] and electromagnetic interference shielding (EMI)^[9]. Three methods of preparing conducting polypyrrole films were previously reported^[10, 11]: chemical polymerization, electrochemical polymerization and chemical vapor deposition (CVD). In recent years, most of this research focused on electrochemical polymerization, but the dimension of electrode restricted the area of PPy film^[12–15]. Chemical polymerization has an advantage over electrochemical method because it is suitable for both conducting and non-conducting substrates and is not restricted by area and surface shape of substrates. Furthermore, chemical method is convenient and rapid.

In this paper, a three-step pretreatment including removing impurities, roughening and silane coupling agent modification of the surface of insulating epoxy resin substrates was carried out first. The pretreatment has

* This work was financially supported by the National Natural Science Foundation of China (No. 60071027).

** Corresponding author: La-zhen Shen (沈腊珍), E-mail: shenlazhen@163.com

Received November 26, 2009; Revised February 5, 2010; Accepted March 2, 2010

doi: 10.1007/s10118-010-9175-x

great influence on the morphology and continuity of PPy films as well as the adhesion between the PPy film and epoxy resin surface. Then, PPy film was chemically polymerized on the surface of epoxy resin in FeCl_3 oxidant solution. The conductivity of PPy films was increased by the addition of dopants, such as I_2 , HClO_4 , sodium dodecyl benzenesulfonate (SDBS), sodium *p*-toluenesulfonate (STS), etc. Doped PPy films obtained in this paper have the ability to shield electromagnetic interference.

EXPERIMENTAL

Materials

The pyrrole monomer (Aldrich, 99%) was distilled prior to use. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Alfa, reagent grade) was used as the oxidant. All other reagents are analytically pure reagent. The insulating reinforced epoxy resin sheet (7 mm $\times$ 7 mm $\times$ 1 mm) was used as substrate in this study. The epoxy resin sheet is the epoxy molding compound (EMC) used in integrated circuit chip, which is provided by Motorola.

Pretreatments on Epoxy Resin Substrate Surface

The epoxy resin substrate was pretreated with three steps. First, the substrate was treated with mixed base solution (mass ratio of $\text{NaOH}:\text{Na}_3\text{PO}_4:\text{Na}_2\text{CO}_3 = 5:2:1$) to remove surface impurities at 70°C for 30 min with gently stirring, and then was washed with distilled water. After drying, the substrate was put in the strong acid roughening solution (the concentration ratio of concentrated $\text{H}_2\text{SO}_4:\text{CrO}_3 = 1:1$) at 85°C for 25 min. Then the substrate was rinsed repeatedly with dilute alkali (10% NaOH), distilled water and absolute alcohol in turn several times, and dried at 60°C. Finally, the substrate was dipped in silane coupling agent aqueous solution (1% *V/V* vinyltriethoxysilane) for 10 min. Subsequently the substrate modified by silane coupling agent was obtained after drying in the air at room temperature.

Polymerization of Polypyrrole Film

Pyrrole monomer (98%, Aldrich) was purified by distillation under reduced pressure prior to use. The pretreated epoxy resin substrate was first dipped in the solution of pyrrole monomer with absolute alcohol as solvent (30% *V/V*). Then, the substrate was immersed into oxidant solution (10% FeCl_3), in which dopant was added. Subsequently, polypyrrole was *in situ* polymerized on the substrate surface to form a PPy film in the above ferric chloride solution. Meanwhile, the color of reaction solution was changed from rust orange to green and finally changed to black. After 30 min, the PPy film was washed with distilled water and absolute alcohol in turn. Finally the resultant film was dried by air at room temperature and the conducting PPy film was obtained.

Measurements

The morphology of the surface of substrate and PPy film was carried out by a Philips XL30 scanning electron microscope (SEM) to obtain SEM images. Infrared spectrum (IR) was taken on a BIO-RAD3000 IR spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurement was made on a PHI-1600 spectrometer with a Mg $K\alpha$ X-ray source. The electrical conductivity of polypyrrole films was measured using a four-point probe instrument (SDY-5). The flange coaxial transmission device (ROHDEA & SCHWARZ) was used to measure the shielding effectiveness of critical frequency points as well as the amplitude-frequency curve of PPy film samples in the frequency range of 30 MHz–1.5 GHz.

RESULTS AND DISCUSSION

The surface of epoxy resin attached with impurities is unclean and has less reactive site, thereby it is difficult for polypyrrole to deposit on the substrate surface. As mentioned above three important factors, such as removing impurities, roughening and surface modification with silane coupling agent, etc., can affect the morphology and adhesion of PPy. These factors were studied and discussed carefully in this paper. The electromagnetic interference shielding effectiveness (SE) is proportional to electrical conductivity according to Schelkunoff theory^[16, 17]. In order to obtain PPy films with high SE value, the factors improving the conductivity of PPy films were investigated.

Effect of Removing Impurities and Surface Roughening

The multi-functional epoxy resin is used as the matrix resin. The phenolic resin as curing agent and SiO_2 as filler in the epoxy resin substrate were used in this paper. The SEM image of substrate surface is given in Fig. 1. The surface with no pretreatment is relatively flat and is covered by the epoxy resin basically (Fig. 1a). When the substrate is roughened, the epoxy resin on the surface is gotten rid of and SiO_2 particles are bared and distributed on substrate surface uniformly (Fig. 1b). The bottom of large diameter SiO_2 particles is still connected with epoxy resin, and the epoxy resin also wraps a large number of the smaller diameter SiO_2 particles. A “ball-Gap” socket structure is formed and increases the roughness, touch area and wetting degree of epoxy resin surface.

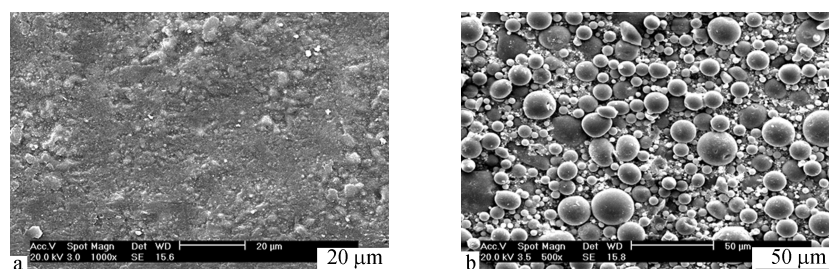


Fig. 1 SEM images of substrate surfaces with (a) no pretreatment and (b) pretreatment by roughening

Figure 2 shows the SEM images of PPy films on the substrate surface. It can be observed that scattered polypyrrole regions deposit on substrate surface after removing impurities, the PPy layer is sparse shown as Fig. 1(a). The removal of impurities increases active centers and leads to more PPy molecules deposit on substrate surface than that obtained without pretreatment. And it makes substrate surface possess positive charges after removing impurities. However, pyrrole monomer also has positive charges by losing an electron to be a radical cation using oxidant. The same electric charges lead to repulsing each other between pyrrole monomer and substrate, which makes less polypyrrole polymerized on the substrates surface.

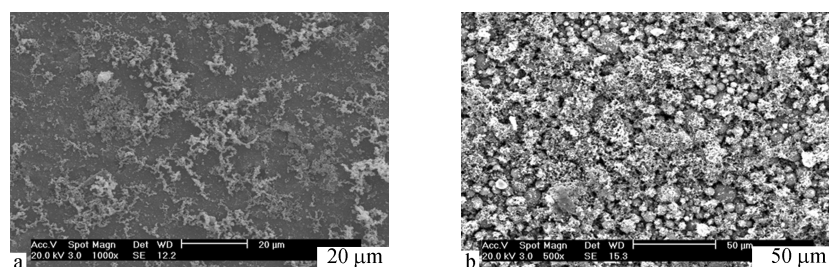


Fig. 2 SEM images of PPy films obtained after surface pretreatment of substrate by (a) removing impurities and (b) roughening

When the substrate surface is roughened, the density of PPy molecules is increasing as shown in Fig. 2(b). A PPy film forms in contrast with the scattered PPy regions shown in Fig. 2(a). The reason is that the roughness, touch area and wetting degree of epoxy resin surface are improved, and many benzene rings exist in the epoxy resin substrate. The negative groups including sulfonic acid groups ($-\text{SO}_3\text{H}$) and hydroxyls ($-\text{OH}$) are introduced in benzene rings from high concentration sulfuric acid of the roughening liquid. These negative groups change the substrate surface to be electronegative. During polymerization reaction, the ion pairs are formed between negative groups ($-\text{SO}_3\text{H}$ and $-\text{OH}$) and pyrrole atomic groups with positive charges, which improve the adhesion between PPy film and substrate. Therefore, pretreatment by removing impurities and surface roughening has obvious effect on adhesion of PPy film.

Effect of Silane Coupling Agent Modification

Figure 2(b) also shows that PPy film can't cover the substrate surface in that the sulfonic acid group and hydroxyl all are hydrophilic groups and repulse the lipophilic polypyrrole. It is necessary to modify the substrate surface to be lipophilic. Through a series of experiments, vinyltriethoxysilane ($\text{CH}_2=\text{CH}-\text{Si}(\text{OC}_2\text{H}_5)_3$), as a kind of silane coupling agent, was chosen to modify the substrate surface in this study. The PPy film polymerized after surface modification is shown in Fig. 3. It is clear that PPy film is more continuous and homogeneous contrast to Figs. 2(a) and 2(b), and the film can cover substrate surface.

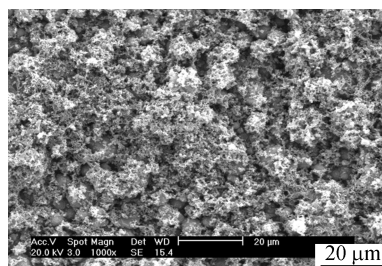


Fig. 3 SEM image of PPy film obtained after surface pretreatment of substrate by silane coupling agent modification

The two ends of vinyltriethoxysilane are different groups. Ethoxy ($-\text{Si}(\text{OC}_2\text{H}_5)_3$) is the head group and vinyl ($-\text{CH}_2=\text{CH}$) is the end group. There is a large number of hydroxyls on SiO_2 on the substrate surface. Ethoxy is hydrolyzed to the active silanol group ($-\text{Si}(\text{OH})_3$), which can react with hydroxyl on SiO_2 , and forms the covalent bond $\text{Si}-\text{O}-\text{Si}$ by the dehydration condensation reaction. Thus, vinyltriethoxysilane can adhere to the substrate surface tightly. The other end vinyl is a lipophilic group with reaction activity, and changes the substrate surface to be lipophilic. On the basis of the theory of “similarity and interattraction”, vinyl and PPy interacts through Van Der Waals force. In addition, there is still a strong electrostatic attraction between negative groups and positive pyrrole atomic groups. The result is that the adhesion between PPy film and epoxy resin surface increases and the PPy film is more continuous and homogeneous.

Effect of Doping

Polypyrrole is a π -conjugated conducting polymer and has helix chain configurations or stacked structures. The dopant is π -conjugated anions as well. The π -conjugated anions can be incorporated fully within the PPy matrix and increase the conjugated chain length of PPy molecules^[18]. The conjugated anions also are retained as the counterions of cations in polypyrrole backbone. The spatial structure stability can be greatly improved. Taking STS-doped and SDBS-doped PPy films as examples, the effect of dopant on morphology of PPy film is shown in Fig. 4. From this figure, it is clear that doped PPy films are more regular, dense and continuous than undoped PPy films.

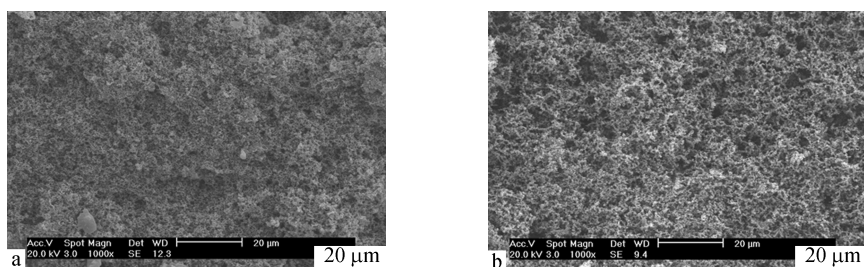


Fig. 4 SEM images of (a) STS-doped and (b) SDBS-doped PPy films

Dopant has great influence on the electrical conductivity of PPy films too. The conductivity can be improved to different extents by doping with different dopants, such as I_2 , $HClO_4$, SDBS, STS, *etc*^[19, 20]. This paper discusses the effect of doping amount on conductivity of SDBS-doped PPy films. Seven doping amounts in the range of 0 g/L to 50.0 g/L were studied. The corresponding conductivities are given in Table 1. It can be seen that conductivities of SDBS-doped samples all are larger than 25 S/cm and have a prominent increase compared with the conductivity (about 8 S/cm) of undoped sample. Moreover, the conductivity of PPy films varies with the increase of doping amount. The conductivity reaches a maximum value (45.10 S/cm) at doping amount 33.0 g/L. When the amount of dopant increases from 0 g/L to 33.0 g/L, the conductivity increases from *ca.* 8 S/cm to 45.10 S/cm, then the samples show a decrease in conductivity when the amount of dopant is higher than 33.0 g/L. Therefore, there is an optimum doping amount corresponding to the maximum conductivity of PPy films.

Table 1. Effect of SDBS doping amount on conductivity of PPy films

Doping amount (g/100mL)	Conductivity (S/cm)
0.00	5–10
0.83	25.85
1.67	32.88
2.50	38.12
3.30	45.10
4.20	39.81
5.00	26.47

The conduction occurs via migration of charge carriers along the conjugated polymer chains and hopping of charge carriers across the conjugated chains^[21]. The conductivity (σ) can be given by the formula:

$$\sigma = \Sigma qn\mu \quad (1)$$

where q is the charge value, n is the concentration of charge carriers and μ is the carrier mobility. Therefore, the conductivity is proportional to concentration of charge carriers and carrier mobility.

Molecular orbital theory indicates that conjugated polymers have conductive capability when charge carriers get across the energy level difference between π occupancy orbit and π^* empty orbit. The energy level difference hinders the moving, hopping and migration of charge carriers between sites on different polymer chains, which can reduce the conductive power of conjugated polymers. In this study, the addition of π -conjugated anions is favorable to increase not only the concentration of charge carriers in PPy chains, but also the conjugated chain length of PPy molecule. The increase in concentration of charge carriers decreases in π - π^* energy level difference and improves carrier mobility effectively. The increase of π -conjugation length of PPy molecules can increase the interchain hopping frequency of carriers, which improves carrier mobility as well. Therefore, conductivity of PPy films increases with the increase of doping amount less than the optimum doping amount. However, excessive doping amount will influence the moving and migration of charge carriers, that makes carrier mobility and conductivity of PPy film decrease. Thus, it shows a decrease in conductivity when the amount of dopant is higher than 33.0 g/L. Taking into accounts all discussion above, the conductivity of SDBS-doped PPy films has a prominent increase to be 45.10 S/cm at an optimum doping amount.

IR Analysis

Figure 5 shows the IR spectra for undoped PPy film (curve a) and STS-doped PPy film (curve b). Both IR spectra show the characteristic absorption bands of PPy in accordance with those reported in previous studies^[22–24]. The two curves all show a strong broad N—H stretching vibration absorption band at 3436 cm^{-1} . The characteristic absorption bands of PPy, the pyrrole ring vibrations, can be observed at 1640, 1541, 1457, 1311 and 1172 cm^{-1} . The bands at 1640 and 1541 cm^{-1} are C=C/C—C stretch peaks of ring stretching modes. The peak at 1457 cm^{-1} corresponds to the C—N stretching vibration in the ring. The bands at about 1311 and 1172 cm^{-1} are ascribed to C—N absorption bands. There is an increase in strength at 3436 and 1640 cm^{-1} and a

decrease in wavenumber at 1311 and 1172 cm^{-1} in curve (b) compared to curve (a). The skeletal vibrations were influenced by doping. The spectra of samples all have no peak at 1710 cm^{-1} attributed to C=O or CH₂ stretching modes, which indicates that neither ring open nor H add in the pyrrole ring. Based on IR spectra, undoped PPy film and STS-doped PPy film all have identical organic backbone structures and consist of mostly undestroyed pyrrole units.

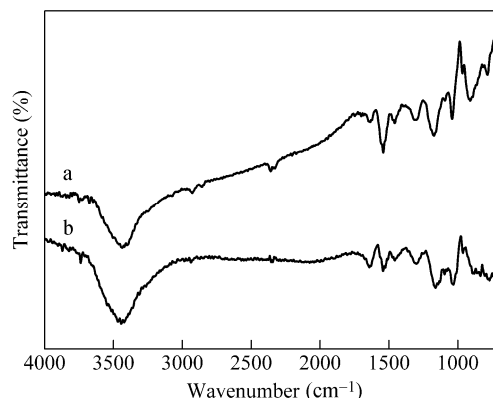


Fig. 5 IR spectra of (a) PPy film and (b) STS-doped PPy film

XPS Analysis

Taking STS-doped PPy film as an example, the XPS spectroscopy is shown in Fig. 6. Parts (a) and (b) of Fig. 6 are the C1s and N1s XPS spectra, respectively. The main C1s peak component can be observed at the low binding energy (BE) of 284.60 eV for the C1s neutral carbon peak in pyrrole ring. Figure 6(a) shows a component peak at 287.86 eV being assigned to C—N. C1s XPS spectra also shows that the presence of a high binding energy shoulder at 291.32 eV. This shoulder is attributed to disorder carbons, shakeup, Fermi level electron excitation and carbonyls^[25]. On the basis of IR spectrum of STS-doped PPy film, the XPS signal at 291.32 eV may correspond to shake-up of benzene rings (inside STS) rather than disorder carbons or carbonyls.

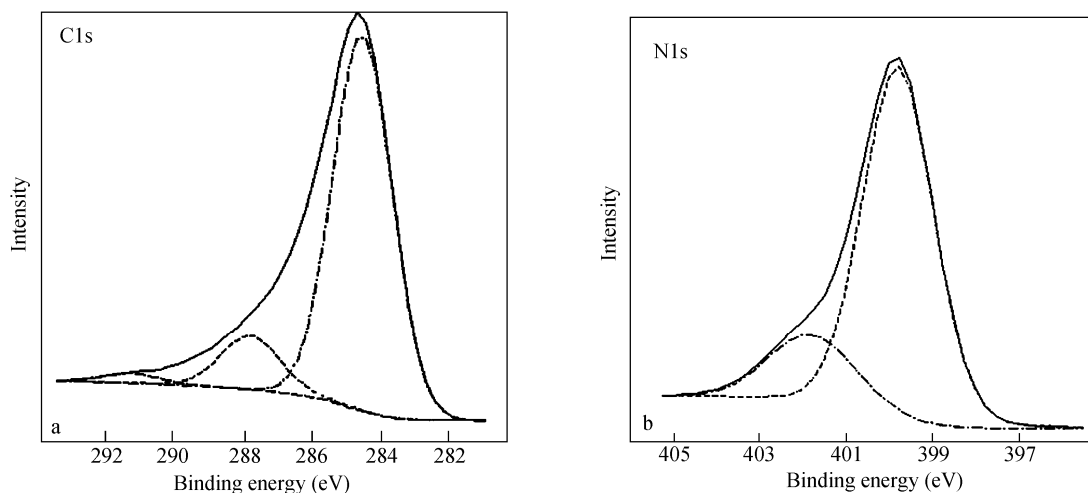


Fig. 6 C1s (a) and N1s (b) XPS spectra of STS-doped PPy film

In Fig. 6(b), there are two component peaks appearing in N1s XPS spectrum. The main component peak at 399.78 eV is assigned to the neutral —NH— nitrogen. The peak of high BE at about 401.86 eV is attributed to positively charged nitrogen (N^+). This indicates that the neutral nitrogen is oxidized to be positively charged nitrogen during polymerization^[26, 27].

EMI SE

The conductivity of the STS-doped PPy film chosen for measuring EMI SE is 28.5 S/cm. The shielding effectiveness as measured by coaxial transmission line method from 30 MHz to 1500 MHz is given in Fig. 7. The figure reveals that EMI SE of about 30 dB for the PPy film sample is obtained. The sample shows a stable SE of 33 dB in the range of 30–200 MHz and 26–30 dB in the range from 200 MHz to 1500 MHz. For most industrial applications, a SE of 30 dB is a useful attenuation value because it will prevent 99.9% of electromagnetic interference^[28]. It can be inferred from this data that the doped PPy film can be used for EMI shielding.

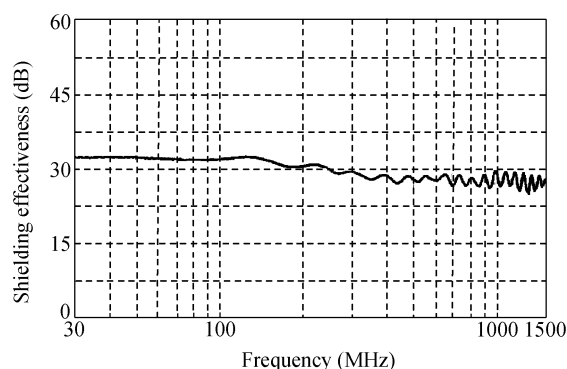


Fig. 7 Shielding effectiveness of STS-doped PPy film in the frequency range 30–1500 MHz

CONCLUSIONS

PPy films with good properties of high conductivity, strong adhesion and high EMI SE were polymerized on the surface of insulating epoxy resin substrates by chemical polymerization from FeCl_3 solution. A variety of methods, SEM, IR, XPS and coaxial transmission line method, were used to investigate the characteristics of the PPy films. The good homogeneity and enhanced adhesion proved that the substrate surface was effectively modified and the adhesion of PPy film was availably enhanced through removing impurities, roughening and silane coupling agent modification. The conductivity of PPy films increased by about one order of magnitude with the addition of dopant. EMI SE of STS-doped PPy film sample was in the practically useful range of about 30 dB over a wide frequency range from 30 MHz to 1500 MHz.

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